

SPECTROSCOPY OF IODONIUM COMPOUNDS

Part II. Xylyl Iodonium Compounds and their Spectra

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Abstract. *o*, *m* and *p*-xylyl iodonium compounds have been prepared and their IR spectra are recorded for the 1600–250 cm^{-1} region. The spectra of these 1,2,4-trisubstituted benzene derivatives are interpreted in terms of the variation in intensity with respect to the substituent positions in the corresponding xylyl halides where there are marked changes for the various vibrations. The UV spectra of the compounds have also been presented. IR and UV spectra both suggest that the iodonium cation in the *p*-xylyl compounds interacts with the π -electrons of the ring more than in the *ortho* and *meta*-xylyl compounds.

The preparation and spectra of a series of iodonium compounds has been reported in the past.^{1–3} We have also reported the IR and UV spectra of multivalent iodine compounds of benzene and toluene.³ Our interest has been centred on the intensity of some X-sensitive vibrations and also some of the skeletal vibrations occurring in the 1300–1600 cm^{-1} region. These studies have so far been limited to mono or disubstituted ring systems. In this paper we wish to report the systems where the aryl group is *o*, *m*, or *p*-xylyl. The preparation of the *o*-xylyl compounds has not been reported previously although they can be obtained by the conventional methods.

Experimental

The xylyl iodonium compounds have been prepared by the treatment of the corresponding xylene with potassium iodate in the acetic acid–acetic anhydride–sulphuric acid system. Iodonium iodide was obtained by adding potassium iodide and the bromide by adding sodium bromide to the resulting mixture. The chlorides could not be obtained in good yield and are not being reported here. The IR spectra were recorded in KBr pellets and by taking weighed amounts of the compound and KBr and recording the spectra so that the maxima remained in the 40–70% absorption range. The integrated intensity data were calculated as described earlier.⁴ The IR spectra were recorded on a Beckman IR-10 spectrophotometer at the University of Western Ontario, London, Canada, under the CIDA–NRC research associateship programme. UV spectra were recorded in methanol on a SP-700 spectrophotometer.

Results

It would be observed from the spectra that no matter which xylene is taken as the starting material, the substitution occurs in such a way that the ring is 1,2,4-substituted. Thus the *ortho*, *meta*- and *para*-xylenes yield a 1,2,4-substituted iodonium compound. It is noted that the position of the bands is not as much sensitive to substitution as is the intensity. In each

case a difference occurs with respect to the intensity of the band at least in the 800–650 cm^{-1} region.

IR Spectra of the Iodo Compounds. The ring system under discussion is for 1,2,4-trisubstituted benzene derivative. For such derivatives Green, Harrison and Kynaston⁵ have given the assignment for the fundamental bands according to which the interpretation of the spectra is quite simple. Assignments for such trisubstituted ring systems are not available except for this reference.⁵ Tables 1–5 furnish the assignments for iodoxylenes like 4-iodo-*m*-xylene (a) 2-iodo-*p*-xylene (b) and 4-iodo-*o*-xylene (c) and also their iodonium compounds. It might be found from the Tables that among the simple iodides and also their iodonium compounds there is a slight variation in the position of the bands. Thus the ν_4 mode occurs at 1605 cm^{-1} in the spectrum of (a) and (b) but at 1590 cm^{-1} in (c). The intensity varies in the respective order noted above. The ν_5 band is not noted in compound (a) and the intensity in (b) and (c) is of the same order. The ν_6 band has a very high intensity in compound (c). This band happens to be the *n* mode which has been found in our earlier studies to absorb intensely, in cases where the neighbouring group effect is operative and is quite predominant in the *o*-tolylphosphonium compounds.⁶ The intensity of this mode is not as high in the other compounds as in compound c. Similarly $\delta_{as} \text{CH}_3$ vibration has also a high intensity in compound c while in the others the intensity is average. The *m* mode or ν_7 absorption occurring at a lower frequency 1376 cm^{-1} than in the tolyl compounds does not have a high intensity again and similar is the case with the *o* mode or ν_8 absorption.

The pattern of absorption in the 1600–1300 cm^{-1} region is such that ν_4 and ν_5 modes have an average intensity while ν_6 is quite high, followed by the $\delta_{as} \text{CH}_3$ absorption. ν_7 is rather different in each case and ν_8 is weak having almost similar absorption intensity. It has been pointed out earlier that for the phosphonium compounds *m* mode absorbs at a slightly higher wave number compared with the arsonium analogues.⁴ The change in position and in intensity has been related to the deactivation of the ring at the *meta* position and in the present case it may be extended to this position with respect to

iodine.⁴ The higher inductive effect of the methyl group placed in the *ortho* position in compound c is sufficient to cause a similar deactivation of the ring which is further deactivated by the induced polarization of the iodine atom. Since the frequency shifts to higher position if the inductive effect is higher, the observed changes are substantiated. It may, however, be mentioned that the intensity changes and the positions are almost the same in compounds (b) and (c) and hence the variation in the *ortho*-xylyl compound must be attributed to steric factors which has been discussed earlier^{4,6} in terms of the neighbouring

group effect. The *o* mode is also found to change its position in the three iodo compounds, which suggests that this is also sensitive to the position of the substituent, since the overall electronegativity of the compounds is the same. The position changes gradually from (a) to (c), where it is the highest. However, the shifts in this position could be due to changes in the positive inductive effect due to changes in the position of the substituents. Consequently this band may be assigned to the X-sensitive mode ν_8 , an assignment justified by the higher intensity of the absorption in compound (c).

TABLE 1. CHARACTERIZATION OF THE XYLYL IODONIUM COMPOUNDS.

Compounds	M.p.	C(%)		H(%)	
		Calcd	Found	Calcd	Found
(<i>o</i> -Xylyl) ₂ I ⁺ I ⁻	134	41.3	41.5	3.88	3.81
(<i>p</i> -Xylyl) ₂ I ⁺ I ⁻	133	41.3	41.04	3.88	3.91
(<i>o</i> -Xylyl) ₂ I ⁺ Br ⁻	165	45.93	45.27	4.35	4.21
(<i>m</i> -Xylyl) ₂ I ⁺ Br ⁻ ·2H ₂ O	168	42.29	42.58	4.84	4.18
(<i>p</i> -Xylyl) ₂ I ⁺ Br ⁻	151	45.93	45.99	4.3	4.23

TABLE 2. IR SPECTRA AND ASSIGNMENT FOR 4-IODO-*o*-XYLENE AND *o*-XYLYL IODONIUM HALIDES.

4-Iodo- <i>o</i> -xylene (c)			<i>(o</i> -Xylyl)I ⁺ Br ⁻ (f)			<i>(o</i> -Xylyl) ₂ I ⁺ I ⁻ (g)			Assignment
Liquid	Solution	Integrated intensities (I)	Solid	Solution	Integrated intensities (I)	Solid	Solution	Integrated intensities (I)	
1605	1590	525	1588	1590	962	1590	1587	1130	ν_4
1558	1515	480		1560	233				ν_5
1471	1477	3120	1480	1475	497	1480	1466	323	ν_6
1433	1433	2900		1443	1245	1450	1443	1506	δCH_3
				1412	1506		1414	2420	δCH_3
1374	1379	589	1388	1383	956	1390	1377	1076	ν_7
1277	1280	98	1290			1295			ν_8
1269			1280	1269	405	1285	1271	592	ν_9
1230			1225			1230			ν_{10}
1133	1136	326	1142	1166	832	1145	1176	753	ν_{11}
1116	1120	218		1114	502	1125		631	ν_{12}
1017	1020	68	1025			1025			ν_{13}
987	990	526	998	989	292	1000	993	4173	CH ₃ rock
849	871	359	872			885			ν_{14}
			832			845			ν_{23}
			823			820			
805		757	805			805			ν_{24}
741			746			748			ν_{15}
693			702			700			ν_{16}
			615			615			ν_{25}
			545			542			ν_{26}
			528			527			
			440			440			ν_{18}
			270			270			ν_{20}

TABLE 3. IR SPECTRA AND ASSIGNMENT FOR 4-iodo-*m*-xylene and *m*-xylyl IODONIUM HALIDES.

4-Iodo- <i>m</i> -xylene (a)			$(m\text{-xylyl})_2\text{I}^+\text{Br}^-$ (h)			$(m\text{-Xylyl})_2^+\text{I}^-$ (i)			Assign- ment
Liquid	Solution	Integrated intensities (I)	Solid	Solution	Integrated intensities (I)	Solid	Solution	Integrated intensities (I)	
1593	1605	166		1595	591		1587	869	ν_4
1468	1479	845		1481	375		1471	850	ν_6
1379	1376	540	1376	1370	583	1364	1370	963	ν_7
1281	1279	37	1266	1258	109	1264	1274	137	ν_8
1271	1274	50							ν_9
1233	1230	71	1232			1229			ν_{10}
1169	1170	81	1190			1186			
1141	1142								ν_{11}
	1120	57							ν_{12}
1039	1032	257	1031		368	1028		567	ν_{13}
				1000			995		
1011	1009	590	998	994	650	997	990	1092	CH_3 rock
	945	54							ν_{22}
921	918	105	916			918			ν_{23}
871	871	220	895	866	45	895	866	160	ν_{14}
			888			883			
						876			
805	805	184	810			809			ν_{24}
723			714			714			ν_{15}
693			685			685			ν_{16}
665									ν_{25}
532									ν_{26}
433									ν_{17}
269									ν_{18}

TABLE 4. IR SPECTRA AND ASSIGNMENT FOR 2-iodo-*p*-xylene and *p*-xylyl IODONIUM HALIDES.

2-Iodo- <i>p</i> -xylene (b)			$(p\text{-Xylyl})_2\text{I}^+\text{Br}^-$ (d)			$(p\text{-Xylyl})_2^+\text{I}^-$ (e)			Assign- ment
Liquid film	Solution	Integrated intensities (I)	Solid in KBr	Solution	Integrated intensities (I)	Solid in KBr	Solution	Integrated intensities (I)	
1600	1605	499	1600	1608	1234	1600	1603	1327	ν_4
1562	1555	491	1540	1524	431	1550			ν_5
1485	1479	1381	1485	1477	1085	1485	1484	862	ν_6 δCH_3
						1450			
1380	1376	327	1382	1374	856	1385	1372	1197	ν_7
1275	1277	54	1272	1273	186	1272			ν_8
1210			1220			1217			

(Continued)

(Table 4 continued)

1148	1148	71	1155	1147	521	1150	1144	456	ν_{11}
1035	1030	488	1045			1025			ν_{13}
1010	1011	91	980	975	156	980	972	863	CH ₃ rock
978	945	49							ν_{12}
			890						
872	873	268	880			880			ν_{14}
848	846		830	861		840	863		ν_{23}
810	809		825			820			ν_{24}
733			738			735			ν_{15}
690			695			690			ν_{16}
670			668			665			ν_{25}
530			528			522			ν_{26}
465			450			452			ν_{17}
432			430			432			ν_{18}
320			328			325			ν_{19}
310			300			280			ν_{28}
265			265			265			ν_{20}

TABLE 5. UV SPECTRA* OF XYLENES AND XYLYL IODONIUM COMPOUNDS.

(a) 4-Iodo- <i>m</i> -xylene	λ_{\max} nm	280	271	264	261	253		
	ϵ	550	738	786	817	833		
(b) 2-Iodo- <i>p</i> -xylene	λ_{\max} nm	280	272	265	258	252		
	ϵ	811	875	789	747	704		
(c) 4-Iodo- <i>o</i> -xylene	λ_{\max} nm	280	271	264	260	254		
	ϵ	314	424	471	518	534		
(d) (<i>p</i> -Xylyl) ₂ I ⁺ Br ⁻	λ_{\max} nm	285					235	219
	ϵ	4180					15859	20408
(e) (<i>p</i> -Xylyl) ₂ I ⁺ I ⁻	λ_{\max} nm	285					232	223
	ϵ	4086					22264	28182
(f) (<i>o</i> -Xylyl) ₂ I ⁺ Br ⁻	λ_{\max} nm	280	270				242	217
	ϵ	3644	5359				17147	16719
(g) (<i>o</i> -Xylyl) ₂ I ⁺ I ⁻	λ_{\max} nm	280	272				241	221
	ϵ	3321	4650				20593	28564
(h) (<i>m</i> -Xylyl) ₂ I ⁺ Br ⁻	λ_{\max} nm	280	270				241	219
	ϵ	4538	6210				20063	20063
(i) (<i>m</i> -Xylyl) ₂ I ⁺ I ⁻	λ_{\max} nm	280	273				242	221
	ϵ	3875	4650				17567	22992

*Recorded in methanol

The band in the 1130–50 cm⁻¹ region changes position within reasonable limits and is assigned to mode ν_{11} . This band has a high intensity in (c) but occurs at a lower frequency at 1136 and is followed by compound (a) at 1142 and in compound (b) at 1148. This again may be attributed to an X-sensitive mode. Mode ν_{12} absorbs at the same frequency and has again a high intensity for compound (c). It may be mentioned that this becomes a symmetric C—H inplane bending vibration because of the substituent at position 4 and this could be the reason for its consistency in all the compounds. The X-sensitive mode ν_{13} or q mode has been found in iodobenzene⁷ at

1060 cm⁻¹. In the xylyl compounds (a), (b) and (c) there is no band in this region. However, a band occurs at 1032 in compound (a) at 1030 in compound (b) and at 1020 in compound (c). The intensity changes from (b) to (a) followed by (c), where it is quite low. This is, assigned to the X-sensitive mode because of its change in position on 'onium compound formation. In each case the methyl rocking frequency is also different. In compounds (a) and (c) there is a singlet in each case, occurring at 1009 and 990 cm⁻¹ respectively with almost similar intensity. In compound (b) there are two weak bands, one at 1011 and the other at 986, the latter having medium intensity but lower than

(a) or (c). This again should be attributed to the changes in the position of the methyl group.

The interesting part of the spectrum of these compounds occurs in the 800–875 cm^{-1} region. There are bands in each case at $871 \pm 1 \text{ cm}^{-1}$ at $845 \pm 1 \text{ cm}^{-1}$ [in (a) it occurs at 831] and at 804 cm^{-1} [in (b) it occurs at 809 cm^{-1}]. The intensity of these bands is quite different, (a) has the lowest intensity of the order of 200, while (b) has medium intensity of the order of 700–1000. The 870 band has a lower intensity among these bands but in compound (a) this has a high intensity, while in compound (b) 809 cm^{-1} band has the highest intensity although comparable with the one at 846 and in compound (c) the 847 cm^{-1} band has the highest intensity followed by the one at 804 cm^{-1} .

The bands in the lower region of the spectrum have all been assigned. These bands are quite consistent and occur around the same position except for the X-sensitive mode ν_{17} whose position changes appreciably.

p-Xylyl Iodonium Compounds. On formation of the 'onium compounds it is noted that there are slight shifts in band position to a somewhat lower frequency. In *p*-xylyl iodonium bromide (d) and iodide (e), for example, the ν_4 band shifts to 1600 cm^{-1} in the solid state but in chloroform solution it occurs at 1608 and 1603 cm^{-1} respectively compared with (b) where this band is noted at 1605 cm^{-1} . The ν_5 band is found at 1540 cm^{-1} in (d) and at 1550 cm^{-1} in (e). The ν_6 mode occurs at 1485 cm^{-1} in each case while the δCH_3 deformation mode is noted at 1450 cm^{-1} in (e) only. It may be mentioned that ν_6 is again a high intensity band in both the cases. The ν_7 band also shifts to a higher frequency and is at 1382 cm^{-1} in (d) and 1385 cm^{-1} in (e). Shifts to higher frequency for this mode suggest interaction of the cation with the ring π -electrons. The ν_8 band is noted at lower frequency in each case at 1272 but the 1210 band is shifted to 1220 cm^{-1} in (d) and 1217 cm^{-1} in (e). The ν_{11} band noted in the iodo compound at 1146 shifts to 1150 cm^{-1} in (e) and to 1155 cm^{-1} in (d). In the solution spectra the frequency from 1600 to 1150 cm^{-1} are found to be slightly shifted, particularly mode ν_5 , while mode ν_{10} is missing. The ν_{11} band is, however, noted in the solution spectra at 1144 cm^{-1} in (e). In the solid state they are noted at 1155 and 1150 cm^{-1} respectively. The shift to higher frequency is consistent with the assignment of this band to an X-sensitive vibration. Furthermore, the greater shift in the bromide is also in accord with the observation in the phosphonium compounds where it was pointed out that induced polarization by the central atom is responsible for the overall positive character of the cation. When there is a decrease in the overall electronegativity of the positive moiety the shifts are to the higher frequency and vice versa. Thus in the bromide the shifts are to higher frequency compared with the iodide having a lower overall electronegativity.

The 1290 or ν_8 band is not observed among these compounds nor in (b) and similar is the case with the ν_{12} band. The ν_{13} mode which occurs in (b) at 1030 is shifted to 1045 in (d) and to 1025 in (e). Since this is also an X-sensitive mode, the shifts in the two directions may be explained as above on the basis of electronegativity differences. The CH_3 rocking mode is also shifted to 980 in both (d) and (e). The ν_{14} band

is shifted from 873 in (b) to 880 in (e) and doublet at 880 and 890 in (d). There is a minor difference in the occurrence of the ν_{23} band but there is a major shift for the ν_{24} band, from 809 to 825 and 820 cm^{-1} for both (d) and (e) respectively. For modes ν_{15} , ν_{16} , ν_{25} and ν_{26} , there are again minor differences and the shifts are usually to lower frequencies indicating that the positive iodonium atom interacts though only weakly with the π -electron density of the benzene ring. This is further supported by the shift of the X-sensitive mode ν_{17} to lower frequency from 465 to 450 in the iodonium compound. For the ν_{18} and ν_{20} modes also there are only minor differences. The ν_{19} and ν_{28} bands which were observed in (b) at 320 and 310 cm^{-1} respectively are noted in the iodonium compounds at 328 and 300 in (d) and at 325 and 280 cm^{-1} in (e).

o-Xylyl Iodonium Compounds. For the *o*-xylyl iodonium bromide (f) and iodide (g) the trend is the same as noted in the previous case. In this case mode ν_5 is missing in the solid state but it appears in the solution spectrum of the bromide (f) only. The ν_6 band which occurs at 1477 in (c) is found in almost the same region in the iodonium compound and in (g) it is shifted to 1466 cm^{-1} in the solution spectrum. The δCH_3 mode occurs in (c) at 1443 cm^{-1} and is at the same frequency in the liquid spectrum of both (f) and (g) but in the solid spectrum it is shifted to a slightly higher frequency of 1450 cm^{-1} . It is also interesting that the δCH_3 symmetric mode is noted in the solution spectra of both (f) and (g). The ν_7 band which occurs in (c) at 1380 is shifted in the solid state spectrum of both (f) and (g) to 1390 cm^{-1} but is almost the same in the solution. The ν_4 band is found to gain in intensity for the iodonium compounds but the ν_6 mode loses intensity and same is the case with the δCH_3 modes. The loss in intensity in these cases seems to be related to the neighbouring group effect. It has been said earlier that the intensity of these two modes is high in the *o*-xylyl iodide (c) compared with (a) and (b). The loss in intensity on formation of iodonium compounds suggests that there is quite a bit of relief in the neighbouring group effect. The loss in δCH_3 intensity suggests that the methyl groups are so oriented that steric interaction is considerably reduced. The ν_7 mode, however, has a higher intensity for the iodonium compounds but in solution this frequency is shifted only slightly to higher wave numbers which indicates that the iodonium cation does not interact to the same extent as in the *p*-xylyl compounds. The ν_8 mode which is already at a higher position compared with the other iodoxylyl compounds is shifted further for the iodonium compounds. This shift again suggests that this is an X-sensitive mode. The ν_9 mode shifts to higher frequencies in the solid state is not observed in the iodo compound but occurs at the same position in the solution spectra of the iodonium halides. Since this is related to a symmetric inplane deformation $\beta(\text{C}-\text{H})$ mode, the occurrence of a medium intensity band shows that the arrangement of the two rings in the iodonium compounds is such as to effect coupling of this vibration. The ν_{11} band which has a high intensity for (c) gains further in (f) and (g). This has been assigned to an X-sensitive mode and hence a shift to a higher

frequency in the iodonium compounds and particularly in the solution spectra supports the assignment. The ν_{12} band gains in intensity among the iodonium compounds. The X-sensitive mode ν_{13} is noted at 1025 in (f) and (g) and is shifted by 5 cm^{-1} compared with (c).

The spectrum for the remaining region is quite similar for the two iodonium compounds (f) and (g). The differences in their position are only slight as compared with the *p*-xylyl compounds. Thus the ν_{14} band which occurs in (d) and (e) at 880 cm^{-1} is found in (f) at 872 but in (g) at 850 cm^{-1} . The ν_{15} band noted in the *p*-xylyl compounds at 735 is noted at 745 cm^{-1} in the *o*-xylyl compounds. The 545 band is a high intensity band and is, therefore, assigned to the ring deformation mode ν_{26} . The ν_{17} mode does not occur in the *o*-xylyl compound but the ν_{18} mode is noted at 440 cm^{-1} . This again is an X-sensitive mode and is shifted to a higher frequency compared with *p*-xylyl iodonium compounds (d) and (e).

m-Xylyl Iodonium Compounds. The spectra of *m*-xylyl iodonium bromide (h) and iodide (i) are also closely similar to those of the *ortho* and *para* compounds, but for differences in the 700 cm^{-1} region. The ν_4 and ν_5 modes are resolved in the solution spectra of the iodonium compounds while ν_5 is not observed in the spectrum of the iodo compound (a). The ν_6 band which occurs in (a) at 1479 is shifted to a higher frequency in (h) with a loss in intensity and to a slightly lower frequency in the solution spectrum of (i). This shift again suggests that the iodonium cation in this case is weakly interacting with the ring π -electrons which is the same as the *o*-xylyl compounds. The methyl deformation frequency is also shifted from 1460 in (a) to 1450 in (h) and 1433 in (i). The region for this absorption remains the same in the KBr spectrum.

The ν_6 or *n* mode has a very high intensity while ν_7 shifts to a lower frequency in both (h) and (i) compared with (a) where it occurs at 1376 again suggesting that the cation is weakly interacting. The ν_8 frequency is shifted to lower frequency from 1274 to 1264 cm^{-1} in each case, while ν_9 does not seem to occur in the iodonium compounds. The ν_{10} mode occurs at the same frequency in (a), (h) and (i). The ν_{11} which has been assigned to X-sensitive mode in the previous cases is not very distinct in these spectra. The ν_{12} mode is also not noted in the iodonium compounds but the ν_{13} mode occurs at almost the same frequency. The CH_3 rocking frequency is also shifted to a slightly lower frequency in both (h) and (i). The ν_{22} frequency is not observed while the ν_{23} occurs in (h) at 916 cm^{-1} and in (i) at 918 cm^{-1} . The ν_{14} is shifted to a higher frequency and is split into a doublet in the case of (h) and triplet in the case of (i). The ν_{24} is also shifted to a higher frequency while ν_{15} is shifted to a lower frequency from 723 to 714 cm^{-1} in each case. The ν_{16} is also shifted from 693 to 685 in the iodonium compounds.

A comparison of the spectra of the iodonium compounds in the $1600\text{--}1300\text{ cm}^{-1}$ region suggests that the neighbouring group effect is not operative in the *o*-xylyl iodonium compounds. The interaction of the iodonium cation with ring π -electrons is weak for the

ortho and *meta*-xylyl compounds but in the *p*-xylyl compounds the cation interacts to a large extent.

UV Spectra. The spectra of compounds (a), (b) and (e) are different from those of their corresponding iodonium compounds (d) to (i). The iodo compounds absorb moderately between $250\text{--}280\ \mu$ with varying intensity. The absorption bands in this region are broad with inflexions at the wavelengths noted in Table 4. In the spectra of the iodonium compounds, on the other hand, there is no absorption between $250\text{--}265\ \mu$ region but two inflexions are noted at 270 and $280\ \mu$ among compounds (f) to (i) while there is only one broad band noted at $285\ \mu$ among (d) and (e). For compounds (f) to (i) there are two high intensities, well separated bands noted at 241 ± 2 and at 219 ± 2 while for compounds (d) and (e) these bands are noted at 232 and 235 and at 219 and $223\ \mu$ respectively. It is noted that the intensity of the bands in the $270\text{--}80\ \mu$ region in the iodonium compounds is approximately 10 times higher. The intensity of the 285 bands among the *p*-xylyl compounds (d) and (e) is higher than for the other iodonium compounds except (h). It is also noted that for (b) the intensity in this region is higher than for (a) or (c). The bromides in general have higher intensity than the iodides. It may be mentioned here that it was also reported in our earlier study³ on the phenyl and *p*-tolyl iodonium compounds that the iodonium compounds have much higher intensity compared with their parent iodo compounds. The intensity noted in the present iodonium compounds is of the same order.

The occurrence of two inflexions among the *o*-xylyl and *m*-xylyl iodonium compounds compared with the single broad band in the spectra of the *p*-xylyl compounds suggests that the charge disturbance in the former compounds is more than in the latter. The ring system of the *p*-xylyl compounds appears to be more conducive to electron delocalization, and that in the *o* and *m* compounds the plane as well as the angle between the plane of the rings is affected on onium compound formation mainly because of the position of the substituents.

The two extra bands noted at $230\text{--}40$ and $217\text{--}23\text{ nm}$ may be assigned to the iodonium ion (with an enhancement in intensity for the iodide ion) and the ring $n \rightarrow \pi^*$ transition respectively. It is significant that both absorptions have higher intensity for the iodides than for the bromides and also that the bromides absorb at a shorter wavelength than the iodides as far as the $217\text{--}23\text{ nm}$ band is concerned. This may be because of the higher electronegativity of the bromide ion which makes the iodonium cation more electron deficient than does the iodide ion and it has been reported that an electron deficient cation such as a carbonium ion absorbs at a shorter wavelength than the corresponding electron rich compound.⁸ This explanation should also be applicable to the shift of the broad band in the $270\text{--}80\text{ nm}$ region to higher wavelength in the case of the *p*-xylyl iodonium compounds. The presence of two electron donor methyl groups in the *para* position makes the *p*-xylyl group electron rich and hence the occurrence of the band at a higher wavelength. As a consequence of the higher electron density of the *p*-xylyl ring and

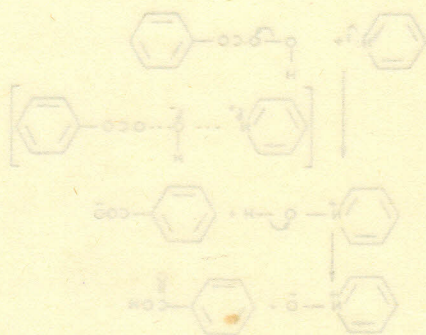
the interaction of the lone-pair on the cation the iodonium ion itself becomes slightly less populated and hence the shift of the 240 nm band to 232–35 nm.

The UV spectra of the *o*-xylyl iodonium compounds are similar to those of the *m*-xylyl compounds but their intensity is lower in the case of the former compounds. The spectra of the *p*-xylyl compounds are different from the others in both position and intensity. It has been seen in the case of the phosphines and arsines that there is a broad band in the 270 μ region corresponding to the $\pi \rightarrow \pi^*$ transition and this is attributed to the interaction of the lone-pair with the ring π -electrons. Such a broad band in the *p*-xylyl compounds should be related to the interaction of the lone-pair on the iodonium cation with the ring π -electrons. The inflexion noted for the *o*- and *m*-xylyl compounds suggest that the charge in the rings is disturbed so that there is a hindrance in the dissipation of energy in the vibrationally excited states of the ring. Such a case would arise due to differences in substituent position which do alter the electron density of the rings. From the IR spectra also it was found that the *ortho*- and *meta*-xylyl iodonium compounds were different from the *p*-xylyl compounds.

The spectral study reported here suggests that although the compounds present a 1,2,4-substituted ring system their spectra differ from one another because of changes in substituent positions, as is indeed expected of isomers. The intensity of the IR bands seem to be particularly sensitive to these changes.

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The oxidation of primary amines to nitroso and nitro compounds of tertiary amines to amine oxides and of secondary amines to nitroso compounds and of nitroso compounds to nitramines by the peroxy acid has been explained.^{1,2}

Experimental

All the solvents were purified by standard procedures. Pyridine (B.D.H. reagent grade, D.P.

Pyridine I-oxide was first obtained in 1935 when pyridine was oxidized with peroxybenzoic acid at room temperature. More recently however, peroxyphthalic and peroxyacetic acids have also successfully been used for the oxidation of pyridine to pyridine I-oxide. Effect of solvent on the kinetics of peroxybenzoic acid oxidation of some common nucleophiles such as aromatic sulphoxides, cyclic ethers and triphenyl phosphine have previously been reported.^{3,4} In continuation of our general interest in such reactions, we have now kinetically examined the system pyridine + peroxybenzoic acid-pyridine I-oxide-benzoic acid in the solvents given in Table 2. Some of these solvents have been used in the previously reported studies. These solvents not only represented a wide range of dielectric constants but were also easily available in pure form and hence their choice. This choice will therefore be helpful in comparing the oxidative behaviour of different nucleophiles in similar environments.

Results and Discussion

The rate constants for the oxidation of pyridine with peroxybenzoic acid were determined using hexane, cyclohexane, chloroform, chlorobenzene, butanol, n-propanol, acetone, ethanol and acetonitrile as the solvents arranged in their ascending order of dielectric constants at 30°C ($\pm 0.2^\circ$ C) and in chloroform alone at 30.0, 40.0, 45.0 and 50.0°C ($\pm 0.2^\circ$ C). The reaction was found to be second order with respect to both the reactants. The energy of activation was calculated from the Arrhenius plot and entropy of activation was worked out as reported previously.⁵ The rate data and other physical parameters for this reaction are recorded in Tables 1 and 2.

A graph of the rate constants versus the reciprocal of the dielectric constant of the solvents gave a straight